#### COMPONENTS:

- Mercury(II) selenite; HgSeO<sub>3</sub>; [14459-36-0]
- Water; H<sub>2</sub>O; [7732-18-5]

### ORIGINAL MEASUREMENTS:

Redman, M.J.; Harvey, W.W.

J. Less-Common Met. 1967, 12, 395-404.

## VARIABLES:

One temperature, probably 293 or 298 K

## PREPARED BY:

Mary R. Masson

#### EXPERIMENTAL VALUES:

A solution in contact with a precipitate of  $HgSeO_3$  was found to contain  $7.83 \times 10^{-4} \text{ mol dm}^{-3} \text{ Hg}^{2+} \text{ and } 1.20 \times 10^{-5} \text{ mol dm}^{-3} \text{ total selenite at pH } 2.2.$ 

The solubility product can be calculated from this as follows (compiler).

At pH 2.2,  $\log \alpha_{\text{L(H)}} = 6.21$  when the acid dissociation constants have the values  $K_1 = 4 \times 10^{-3}$  and  $K_2 = 1.0 \times 10^{-8}$  (ref. 1). Then, since  $[SeO_3^{2-}] = [Se_{tot}]/\alpha_{L(H)} = 7.36 \times 10^{-12}$ , and  $[Hg^{2+}] = 7.83 \times 10^{-4}$  mol dm<sup>-3</sup>,  $K_{SO} = 5.76 \times 10^{-15}$  mol dm<sup>-6</sup>.  $(pK_{e0} = 14.24.)$ 

The temperature of the determination is not stated.

# AUXILIARY INFORMATION

# METHOD APPARATUS/PROCEDURE:

A solution of 0.02M  $\mathrm{Hg(NO_3)_2/0.01M\ HNO_3}$  was mixed with a 0.05M solution of  $K_2SeO_3$ . precipitate was filtered off and the filtrate was analysed for mercury(II) and total selenite. Mercury(II) was determined with dithizone, and selenite by means of the reaction with 3,3'-diaminobenzidine.

# SOURCE AND PURITY OF MATERIALS:

Not stated.

## ESTIMATED ERROR:

Errors of  $^{\pm}$  1% in the determination of Hg<sup>2+</sup> and selenite, and an error of  $^{\pm}$ 0.1 unit in the determination of pH would cause an error of approx.  $\pm 2.5 \times 10^{-15}$  in  $K_{\rm SO}$  ( $\pm 0.2$  in pK)

# REFERENCES:

1. Rumpf, P. Compt. Rendu 1933, 197, 686.

## 

## EXPERIMENTAL VALUES:

TIME THE					2		
	All concentr	ations are	expressed in u	nits of m	ol dm <sup>-3</sup> .		
[Na <sub>2</sub> SeO <sub>3</sub> ]	Solution	HgS	[Hg(SeO <sub>3</sub> )2 <sup>-</sup> ]	''K''	[Se03 <sup>2-</sup> ] <sup>a</sup>	$K_{s2}^{a}$	
(total)	wt., g	found, g	x 10 <sup>2</sup>	x 10 <sup>2</sup>	(free)	x 10 <sup>2</sup>	
2.0	5.7554 3.4477	0.2762 0.0640	8.35	4.18	1.92	4.36	
1.0	4.6239 9.3640	0.0462 0.0911	4.25	4.25	0.96	4.44	
0.5	7.5800 9.6050	0.0381 0.0471	2.14	4.28	0.48	4.47	
0.25	7.5130 7.2401	0.0288 0.0264	1.61	(6.44)	0.23	(6.88)	
0.125	6.8250 9.4330	0.0151 0.0214	0.97	(7.76)	0.115	(8.41)	

a Calculated by compiler.

0.0625

The mean value of  $K_{\rm S2}$  is 4.42 x  $10^{-2}$ 

9.7856

7.4048

 $pK_{s2} = 1.35$ 

Note:  $K_{s2} = [Hg(SeO_3)_2^2]/[SeO_3^2]$ , "K" =  $[Hg(SeO_3)_2^2]/(total\ selenite)$ 

0.0121

0.0098

#### AUXILIARY INFORMATION

# METHOD APPARATUS/PROCEDURE:

Solutions of sodium selenite of various concentrations were saturated with mercuric selenite at  $25^{\circ}\text{C}$ . Samples of the saturated solutions were diluted, raised to boiling, then 1-2 g of potassium cyanide was added, and the boiling continued for 5 min. Hydrogen sulfide was passed into the solutions until all the mercury had been precipitated, then the mercuric sulfide precipitates were collected on Gooch crucibles and weighed.

## SOURCE AND PURITY OF MATERIALS:

0.55 (8.80) 0.057 (9.65)

Mercuric selenite was prepared by mixing solutions of sodium selenite and mercuric nitrate.

## ESTIMATED ERROR:

The differences between the duplicate determinations range from 2.3 to 7.2%.

REFERENCES:

#### COMPONENTS: ORIGINAL MEASUREMENTS: Mercury(II) selenite; HgSeO<sub>3</sub>; [14459-36-0] Toropova, V.F. Nitric acid; HNO3; [7697-37-2] 2. Zh. Neorg. Khim. 1957, 2, 515-22; Russ. J. Inorg. Chem. (Eng. Trans1.) 1957, 2, 3. Sodium nitrate; NaNO3; [7631-99-4] 63-76. 4. Water; H<sub>2</sub>O; [7732-18-5] VARIABLES: PREPARED BY: HNO3 concentration Mary R. Masson One temperature: 298 K

#### EXPERIMENTAL VALUES:

All concentrations are expressed in units of mol dm $^{-3}$ . pH [Hg $^{2+}$ ] [SeO $_3^{2-}$ ]a  $K_{SO}^a$ , mol $^2$ dm $^{-6}$  [SeO $_3^{2-}$ ]b  $K_{SO}^b$ ,mol $^2$ dm $^{-6}$  1.00 9 x 10 $^{-4}$  1.6 x 10 $^{-11}$  1.4 x 10 $^{-14}$  2.31 x 10 $^{-12}$  2.08 x 10 $^{-15}$  1.26 5 x 10 $^{-4}$  2.7 x 10 $^{-11}$  1.6 x 10 $^{-14}$  4.16 x 10 $^{-12}$  2.08 x 10 $^{-15}$  1.30 4.7 x 10 $^{-4}$  3.1 x 10 $^{-11}$  1.4 x 10 $^{-14}$  4.70 x 10 $^{-12}$  2.21 x 10 $^{-15}$ 

a Results quoted by author; constants for  $\rm H_2SeO_3$ ,  $K_1 = 3.5 \times 10^{-3}$ ,  $K_2 = 5 \times 10^{-8}$  b Results recalculated by compiler; constants for  $\rm H_2SeO_3 - K_1 = 2.63 \times 10^{-3}$ ,  $K_2 = 1.0 \times 10^{-8}$  (Ref. 1).

The average value for  $K_{\rm SO}$ , as calculated by author, is 1.45 x  $10^{-14}$  mol<sup>2</sup> dm<sup>-6</sup> The average value for  $K_{\rm SO}$ , as recalculated by compiler, is 2.16 x  $10^{-15}$  mol<sup>2</sup> dm<sup>-6</sup> (p $K_{\rm SO}$  = 13.84 and 14.67).

Note  $[Se_{tot}] = [Hg^{2+}]$  and  $[SeO_3^{2-}] = [Se_{tot}]/\alpha_{L(H)}$ where  $\alpha_{L(H)} = (1 + [H^+]/K_2 + [H^+]^2/K_1K_2)$ 

# AUXILIARY INFORMATION

# METHOD APPARATUS/PROCEDURE:

A 1M solution of sodium nitrate, acidified with nitric or sulfuric acid, was saturated with mercury selenite by shaking at  $25 - ^+$  0.05°C until equilibrium was established (after 6 hr). The solution was analysed for mercury polarographically, after separation of selenium as the element.

# SOURCE AND PURITY OF MATERIALS:

A small excess of sodium selenite was reacted with a solution of mercuric nitrate. The precipitate was washed with distilled water, and dried at 105°C. Selenium was determined polarographically as the selenosulfate ion after precipitation as the element, and mercury gravimetrically the sulfide after separation of the selenium.

#### ESTIMATED ERROR:

The spread in the results for  $pK_{\odot}$  is 0.04 of a log unit. Temperature:  $\pm 0.05~\rm K$ 

# REFERENCES:

 Sabbah, R.; Carpeni, G. J. Chim. Phys. 1956, 63, 1549.

## COMPONENTS:

- Mercury(II) selenite; HgSeO<sub>3</sub>; [14459-36-0]
- Sodium selenite; Na<sub>2</sub>SeO<sub>3</sub>; [10102-18-8]
- 3. Sodium nitrate; NaNO<sub>3</sub>; [7631-14-5]
- 4. Water; H<sub>2</sub>O; [7732-18-5]

Toropova, V.F.

ORIGINAL MEASUREMENTS:

Zh. Neorg. Khim. 1957, 2, 515-22; Russ. J. Inorg. Chem. (Eng. Trans1.)  $\underline{1957}$ , 2, 63-76.

#### **VARIABLES:**

Sodium selenite concentration

# PREPARED BY:

Mary R. Masson

#### EXPERIMENTAL VALUES:

All concentrations are expressed in units of mol  $dm^{-3}$ . The results presented here were read from the author's Fig. 2 by the compiler. the  $-\log C$  axis is labelled as follows (at equal spacings): 1.8, 2.0, 2.2, 2.3, 2.4, 2.6, Thus it is not certain whether the data presented here are correct.

-log A	-log <i>C</i>
0.71	2.0
0.975	2.205
1.20	2.305
1.295	2.345
1.62	2.515
2.0	2.815

The author calculated that the log of the formation constant of  $Hg(SeO_3)^{2-}_2$  is 12.48, whence, since  $pK_{s0} = 13.84$ ,  $pK_{s2} = 1.36$ . However, the slope of the graph is not, as stated by the author, close to 1, especially when the data are replotted on a correctly labelled graph. It is not at all clear just how the data should best be interpreted.

$$-\log A = -\log [SeO_3^{2-}]$$
  
 $-\log C = -\log [Hg(SeO_3)_2^{2-}]$ 

#### AUXILIARY INFORMATION

# METHOD APPARATUS/PROCEDURE:

Solutions of ionic strength equal to unity, containing varying concentrations of sodium selenite and sodium nitrate were saturated with mercuric selenite, by shaking at 25 ± 0.05°C until equilibrium was established. The complex ion concentration,  $C_{\mathrm{M}}$ , was taken as equal to the total concentration of mercury ions in the saturated solution (determined The equilibrium polarographically). selenite concentration was calculated from the total concentration.

## SOURCE AND PURITY OF MATERIALS:

A small excess of sodium selenite was reacted with a solution of mercuric The precipitate was washed with distilled water, and dried at 105°C. Selenium was determined polarographically as the selenosulfate ion after precipitation as the element, and mercury gravimetrically as the sulfide after separation of the selenium.

## ESTIMATED ERROR:

No estimates possible.

### REFERENCES: